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Further Studies on a Lead Standard Cell

A DISSERTATION

PRESENTED TO THE GRADUATE COUNCIL OF THE OHIO STATE UNIVERSITY IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

BY

MELVIN GUY MELLON, B.S., M.Sc.

COLUMBUS, OHIO
1919

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COLUMBUS.

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FURTHER STUDIES ON A LEAD STANDARD CELL.*

Part I. Introduction.

A. General.—It is now well recognized that there is neither a large number nor a wide variety of types of arrangements suitable for the chemical combination known as a standard cell, the important, ultimate standard employed in the establishment of the unit for the intensity factor of electrical energy (electromotive force)—the volt.

The requirements for such combinations have been pointed out at various times, and many efforts have been made to select the most satisfactory ones.[1] For their construction Hulett[2] and his co-workers conclude that, in addition to mercury, "zinc and cadmium are the only two metals which fulfil the (required) conditions,"—and, "it is improbable that the other metals will be found of service in standard cells."

Hulett[2] gives the solubility of lead in mercury as 1.3%. From a consideration of this fact and of the other factors enumerated by him as determining the availability of certain metals for use in the construction of standard cells, it would seem that a lead amalgam and lead sulfate might replace the cadmium amalgam and cadmium sulfate in the cadmium cells. Further, Puschin[3] has shown the constancy of electromotive force of lead amalgams of widely different compositions. However, if one attempts the substitution of lead for cadmium, as just suggested, for the construction of an analogous lead cell, difficulties are encountered. Lead sulfate, in contrast to cadmium sulfate, is a slightly soluble salt, as is also the mercurous sulfate. Because of the hydrolysis of the latter in such an arrangement, the results are unsatisfactory. Hulett[2] has shown, in his method for preparing mercurous sulfate electrolytically, that a concentration of sulfate ions as great as that in one to six sulfuric acid must be present to prevent hydrolysis. Saturation with sodium sulfate

* Some material not appearing in the original journal article has been added in this reprint in order to include certain specific details of manipulation.

[1] A complete bibliography is too extensive to mention here, but the following will furnish the important references: Jaeger, "Die Normalelemente," (1902); Abegg-Auerbach-Luther, "Measurement of Electromotive Forces of Galvanic Cells with Aqueous Electrolytes" (Bibliography to 1910); "Bulletins of the Bureau of Standards." Reports of the Physikalisch-Technische Reichsanstalt; Reports in *Bull. Soc. Intern. Elect.; Chem. Abs.*—Decennial Index, p. 2550 (Work from 1907 to 1917); Certain references not included above; Carhart and Hulett, *Trans. Am. Electrochem. Soc.* **5**, 59 (1904); Carhart and Hulett, *ibid.*, **6**, 109, 118, (1904); Wolff, *ibid.*, **5**, 49 (1904); Hulett, *ibid.*, **7**, 733 (1905), **9**, 239 (1906); Wilsmore, *Z. Electrochem.*, **10**, 685 (1904); Steinwehr, *ibid.*, **12**, 578 (1906); Reinders, *Z. physik. Chem.*, **42**, 238 (1903); Barnes, *J. Phys. Chem.*, **4**, 339 (1900); Barnes and Lucas, *ibid.*, **8**, 196 (1904); Comm. Report, *Chem. News*, **90**, 225 (1904).

[2] *Trans. Am. Electrochem. Soc.*, **14**, 65 (1908); *J. Am. Chem. Soc.*, **38**, 20 (1916).

[3] *Loc. cit.*

of the solution in the cell suggested herewith appears to have the desired effect from the standpoint of constancy and reproducibility of results.

In an earlier paper[1] there were presented the results of certain work done in this laboratory upon a lead cell, consisting of the arrangement

$$Pb.Hg \mid PbSO_4 \parallel Na_2SO_4.10H_2O \parallel Hg_2SO_4 \mid Hg,$$

in which Pb.Hg represents a saturated amalgam,[2] and $Na_2SO_4.10H_2O$ represents a solution in equilibrium with an excess of sodium sulfate decahydrate. (Similar cells, using unsaturated amalgams, were also studied; but such cells, although sufficiently constant, are not easily reproducible since their electromotive force is a function of the concentration of the lead in the amalgam.) Because of its constancy, ready reproducibility, and small temperature coefficient, this cell was suggested as a possible standard of electromotive force. The essential chemical reaction of the cell seems to be represented by the equation

$$Pb + Hg_2SO_4 \longrightarrow PbSO_4 + 2Hg,$$

in which the sodium sulfate does not function directly, but merely affects the solubility and the ionization of the sulfates of lead and mercury. This cell resembles the one studied by Babinski,[3] having the arrangement

$$Pb.Hg \mid PbCl_2 \parallel 0.25\ N\ HCl + N\ NaCl \parallel Hg_2Cl_2 \mid Hg.$$

B. Object of the Present Investigation.—In the earlier work preliminary experiments with cells containing potassium sulfate instead of sodium sulfate indicated that the former salt could not be used in such a combination. Since the above type of cell differs from the Weston and the Clark cells in that it contains one more solid phase and one more component, and since it may offer, therefore, a possibility of some secondary reaction, such as the formation of a double salt, the present work was undertaken, having as its object (1) the determination of the effect on the electromotive force of the cell arising from the substitution for the component mentioned above, of other components, such as would be supplied with the use of other well-defined, soluble sulfates; and (2) an inquiry concerning the possible cause for any difference between the electromotive forces of the cell containing sodium sulfate and those containing the other sulfates.

[1] Henderson and Stegeman, *J. Am. Chem. Soc.*, **40**, 84 (1918).

[2] Gouy, (*J. physique*, **4**, 320)), gives the solubility of lead in mercury as 1.3%. As noted previously, Puschin has shown that amalgams containing between 1.8% and 66% exhibit the same electromotive force; and Fay and North state that amalgams containing between 2% and 55% are 2-phase systems, consisting of a granular phase of constant composition (Pb_2Hg), and a liquid phase which has also a definite composition when equilibrium is reached.

[3] Dissertation, Leipzig, 1906.

Cells were constructed, therefore, using not only sodium sulfate, but also, in its stead, the well-defined, soluble sulfates of potassium, lithium, magnesium, nickel, cobalt, zinc, manganese, cadmium, and copper. The following pages present an account of the experimental methods employed, the measurements made together with a discussion of them, and the results of work done because of certain observations made during the earlier part of the investigation.

Part II. Experimental.

A. Apparatus.—The apparatus used was essentially the same as that employed in the earlier work. The measurements were made by the compensation method, using a potentiometer reading to 0.00001 volt, in connection with a correspondingly sensitive galvanometer. A lead accumulator furnished the compensating current, and 2 certified Weston standard cells, recently checked, served as references. All measurements were made at $25.0° \pm 0.01°$, as indicated by a thermometer standardized by the Bureau of Standards.

B. Source and Purification of Materials.—The original materials used for the preparation or the purification of the final compounds or metals were the best obtainable. Conductivity water[1] was used throughout the work for the preparation of solutions, recrystallization of salts, etc. The mercury was purified by the methods of Hildebrand[2] and of Hulett.[3] The mercurous sulfate was prepared by the method of Hulett.[4] Two recrystallizations were made on the lead nitrate.[5] Lead sulfate was prepared as before[6] and preserved under dil. sulfuric acid.

The lead amalgams were prepared electrolytically, following somewhat the method of Goodwin.[7] In a small crystallizing dish were placed 2 porcelain crucibles. In one was a weighed amount of mercury (30 to 50 g.) under the surface of which dipped a platinum wire sealed into a glass tube, the whole serving as a cathode. In the other a circular anode of platinum foil about 2.5 cm. in diameter was suspended horizontally half way from the bottom. The dish was nearly filled with a 10% solution of lead nitrate, covering the crucibles. A current of approximately 40 milliamperes from a large storage cell served for the electrolysis. Assuming that the deposition of lead follows Faraday's law, 2 coulometers were placed in the circuit, a water coulometer to indicate when the

[1] Moseley and Meyers, *J. Am. Chem. Soc.*, **40**, 1409 (1918).

[2] *Ibid.*, **31**, 933 (1909).

[3] *Phys. Rev.*, **33**, 307 (1911).

[4] *Ibid.*, **32**, 257 (1911).

[5] Baxter, *J. Am. Chem. Soc.*, **37**, 1027 (1915); Richards and Lembert, *ibid.*, **36**, 1332 (1914).

[6] Henderson and Stegeman, *loc. cit.*

[7] *Z. phys. Chem.*, **13**, 596 (1894).

approximately desired deposition should have taken place, and a copper coulometer for the more exact determination.[1]

The soluble sulfates were recrystallized twice. Only the forms stable at room temperatures were desired and the conditions followed to obtain these forms are outlined below under the individual salts.

a. Sodium Sulfate, $Na_2SO_4.10H_2O$.—A supply of crystallized salt was twice recrystallized, Richards and Yngve[2] having shown that it is readily obtained in a very pure state by recrystallization. The salt was preserved in a moistened condition.

b. Potassium Sulfate, K_2SO_4.—The potassium sulfate was recrystallized rather rapidly by heating to hasten evaporation.[3] It separates in hard crystals without water of crystallization, as no hydrates are known.[4]

c. Lithium Sulfate, $Li_2SO_4.H_2O$.—On keeping concentrated solutions of lithium sulfate heating, a needle like form separates—probably the anhydride.[5] Slow evaporation was used, therefore, to obtain the desired monoclinic plates.

d. Nickel Sulfate, $NiSO_4.7H_2O$.—In order to be certain of obtaining the heptahydrate of nickel sulfate evaporation at room temperatures was used. The heptahydrate, if left in contact with its saturated solution above 54°, is converted into green monoclinic crystals with six molecules of water. It was preserved slightly moistened since long exposure brings about a slight change to the hexahydrate.[6]

e. Zinc Sulfate, $ZnSO_4.7H_2O$.—Jaeger[7] has pointed out the necessity of obtaining the heptahydrate of zinc sulfate for satisfactory Clark cells. The hexahydrate separates on evaporation above 50°.[8] Therefore, the method of Hulett[9] was followed carefully, making one more recrystallization at room temperature. Three recrystallizations were used for the very accurate work of Lee.[10]

f. Cadmium Sulfate, $CdSO_4.8/3H_2O$.—Evaporation at room temperature was used for cadmium sulfate according to the method of

[1] The validity of this assumption is now the object of a further investigation. A relatively thick coating of lead peroxide always formed on the anode, and the solution became distinctly acid. Since amalgams containing between 2 and 60% of lead show the same potential, the present work is unaffected by this uncertainty, except for some question regarding the exact percentage of lead in the amalgams. All those used contained a solid phase.

[2] *J. Am. Chem. Soc.*, **40**, 164 (1918).

[3] Carbeth, *J. Phys. Chem.*, **2**, 300 (1898).

[4] Abegg, "Handbuch Inorg. Chem.," I, 377 (1908).

[5] *ibid.*, I, 138 (1908).

[6] Roscoe and Schorlemmer, "Treatise on Chem.," II, 1309 (1913).

[7] *Wied. Ann.*, **63**, 354 (1897).

[8] Roscoe and Schorlemmer, p. 657 (1913).

[9] *Phys. Rev.*, **32**, 266 (1911).

[10] Lamb and Lee, *J. Am. Chem. Soc.*, **35** 1666 (1913).

Hulett.[1] The salt seems to be isomorphous with no other known salt, and Hulett has noted the efficiency of the process of purification.

g. Magnesium Sulfate, $MgSO_4.7H_2O$.—Magnesium sulfate heptahydrate in contact with saturated solutions passes into the hexahydrate above 48°, separating from hot, concentrated solutions as non-deliquescent crystals.[2] In the present work crystals were obtained at room temperature by saturating a solution at about 60° and allowing to cool. Purification by recrystallization was used by Lee[3] and by Harkins and Paine.[4]

h. Cobalt Sulfate, $CoSO_4.7H_2O$.—Solutions of cobalt sulfate, standing at 40° to 50° deposit monoclinic crystals of the hexahydrate. Evaporation at room temperature yields the heptahydrate in the form of red prisms which are unalterable in the air.[5]

i. Manganese Sulfate, $MnSO_4.5H_2O$.—Some difference of opinion exists regarding the stability of the various hydrates of manganese sulfate. Some think it is the pentahydrate that separates at ordinary temperatures, while others state it is the tetrahydrate. The former includes Roscoe and Schorlemmer,[6] Friend,[7] and Cottrell.[8] Linebarger[9] maintains that the tetrahydrate separates at ordinary temperatures, and Friend states also that this salt crystallizes out of solution between 25° and 31°. The solutions were evaporated between 20° and 25° to obtain the salt for the present work.

j. Copper Sulfate, $CuSO_4.5H_2O$.—A solution of commercial copper sulfate was boiled with pieces of copper[10] and then with lead peroxide[11] to convert ferrous iron to ferric, since the former salt of iron is isomorphous with cupric sulfate, while the latter is not. The solution was then filtered and the blue, triclinic crystals containing five molecules of water obtained by crystallization from warm, saturated solutions on cooling.

C. Construction of Cells. (*a*) **Saturated Cells.**—In the case of all saturated cells, the paste was prepared and the cell constructed, in general, according to the method of Henderson and Stegeman. The following should be added: the excess solution of lead nitrate in the crucible over the amalgam was displaced by water and then by the solution of the sulfate being used for the cell. Some of the latter solution remained over the amalgam until its transfer to the cell in order to prevent oxidation.

[1] *Loc cit.*

[2] Roscoe and Schorlemmer, "Treatise on Chem.," II, p. 634 (1913).

[3] *Loc. cit.*

[4] *J. Am. Chem. Soc.*, **41** 1158 (1919).

[5] *Roscoe and Schorlemmer*, "Treatise on Chem.," II, 1285 (1913).

[6] *Ibid.*, p. 1150.

[7] "Text-book Inorg. Chem.," VIII, p. 307 (1915).

[8] *J. Phys. Chem.*, **4**, 637 (1900).

[9] *Am. Chem. J.*, **15**, 225 (1893).

[10] McIntosh *J. Phys. Chem.*, **2**, 189 (1898); Carveth *ibid.*, **2**, 300 (1898).

[11] Henderson "Inorg. Preparations" (unpublished).

(*b*) **Unsaturated Cells.**—No solid, soluble sulfate was used in the paste in the unsaturated cells, and the saturated solutions of sodium sulfate, etc., used above were replaced by solutions which had been saturated at 20°, this temperature being below that prevailing in the laboratory.

D. Experimental Data. (*a*) **Preparation of Amalgams.**—From the weight of copper deposited in the copper coulometer was calculated the equivalent weight of lead which should have been deposited in the mercury cathode. This weight, together with the weight of mercury taken, formed the basis for the calculation of the percentage of lead in the amalgams.

(*b*) **Determination of the Electromotive Force of Cells of the Saturated Type.**—In reporting the results of the measurements made it is not possible to include all of them, since 80 new cells measured over the period of time studied resulted in a large number of individual determinations. Table I shows a typical series of measurements for one of the salts, nickel sulfate. It is also representative of the results for all cells showing a constant electromotive force. The time required for the attainment of equilibrium, as indicated by the constancy of electromotive force, varied widely. The cells containing zinc sulfate, for example, were constant in 4 days after their preparation, while those containing potassium sulfate never became constant.

TABLE I.—CELLS CONTAINING NICKEL SULFATE, $NiSO_4.7H_2O$.

Made March 11, 1919. Temp. 25°. Amalgam, 3.50% lead.

Date. 1919.	E. m. f.		
	No. 18.	No. 19.	No. 20
March 12	0.96465	0.96467	.....
March 13	0.96465	0.96465	0.96465
March 14	0.96470	0.96467	0.96470
March 21	0.96465	0.96465	0.96465
April 1	0.96466	0.96466	0.96466
April 16	0.96465	0.96466	0.96466
April 30	0.96465	0.96466	0.96466
May 3	0.96465	0.96466	0.96466
May 24	0.96465	0.96466	0.96466
May 30	0.96465	0.96466	0.96466

Table II contains a summary of the results obtained for the saturated cells. The value recorded for the observed electromotive force, for cells showing a constant electromotive force, is the value maintained during the period of observation; while for those not showing constancy, it is an average of the values observed after the cells were a week old. The electromotive force of cells containing cadmium sulfate showed a rather consistent increase over the period of observation; but those containing

TABLE II.—SATURATED CELLS.

No.	Soluble sulfate.	% Pb in amalgam.	Period of observation.	Observed e. m. f. Volts.	Average variation. Volts.
1.....	$Na_2SO_4.10H_2O$	....	2 yr. 4 mo.	0.96466	±0.00002
			Days		
2.....	$Na_2SO_4.10H_2O$	3.15	90	0.96466	0.00002
3.....		3.08	14	0.96466	0.00002
4.....		3.08	90	0.96466	0.00002
5.....		3.08	14	0.96466	0.00002
6.....		3.23	7	0.96465	0.00002
7.....		3.23	20	0.96465	0.00002
8.....		3.23	7	0.96466	0.00002
9[a].....	K_2SO_4	3.02	90	1.0300	0.005
10.....		3.02	90	1.0270	0.008
11.....		3.02	90	1.0260	0.010
12[a].....	$Li_2SO_4.H_2O$	2.98	75	0.9620	0.0010
13.....		2.98	75	0.9615	0.0007
14.....		2.98	75	0.9620	0.0005
15[a].....	$MgSO_4.7H_2O$	2.84	60	0.9608	0.0008
16.....		2.84	60	0.9600	0.0007
17.....		2.84	60	0.9610	0.0010
18[a].....	$NiSO_4.7H_2O$	3.50	80	0.96465	0.00001
19.....		3.50	80	0.96466	0.00001
20.....		3.50	80	0.96466	0.00001
21.....	$CuSO_4.5H_2O$	3.16	21	0.3489	0.0003
22.....		3.16	21	0.3490	0.0003
23.....		3.16	21	0.3489	0.0003
24.....	$CdSO_4.^8/_3H_2O$	3.58	30	0.9520	0.0010
25.....		3.58	30	0.9540	0.0012
26.....		3.58	30	0.9535	0.0012
27.....	$ZnSO_4.7H_2O$	3.56	30	0.96480	0.00001
28.....		3.56	30	0.96479	0.00001
29.....		3.56	30	0.96480	0.00001
30.....	$MnSO_4.5H_2O$	3.39	30	0.96478	0.00001
31.....		3.39	30	0.96478	0.00001
32.....		3.39	30	0.96479	0.00001

[a] Duplicate sets showed similar results.

magnesium or lithium sulfates did not, and in the case of potassium sulfate, the values varied widely from day to day.[1]

Since the original combination was suggested as a possible standard of electromotive force, it was particularly desirable to obtain some measurements on the cells prepared 2 years earlier. Unfortunately, owing to faulty sealing, only one cell was found to be in good condition, the others having evaporated to such an extent that the electromotive force exhibited was unreliable. The one cell was measured along with the new ones, and it is noteworthy that its value practically coincided with those of the new ones containing sodium sulfate. The results for the latter cells

[1] There was marked evidence of hydrolysis of the mercurous sulfate in the cells containing potassium sulfate, as shown by the appearance of the yellowish, basic salt, after they had been constructed a day.

indicated a verification of the earlier results. This undoubtedly points to a marked constancy, but further data is desirable on the question of constancy for a long period of time.

Neither ammonium sulfate nor calcium sulfate was of value for cells. The former reacts with mercurous sulfate; and the latter, because of its small solubility, does not prevent the hydrolysis of the same salt of mercury.

(*c*) **Determination of the Electromotive Force of Cells of the Unsaturated Type.**—Jaeger[1] has shown that Clark cells containing more than one hydrate of zinc sulfate exhibit considerable variation from the

TABLE III.—UNSATURATED CELLS.

No.	Soluble sulfate.	% Pb in amalgam.	Period of observation. Days.	Observed e. m. f. Volts.	Average variation. Volts.
1[a]	Na_2SO_4	3.58	55	0.96466	±0.0004
2				0.96466	0.0003
3				0.96466	0.0002
4	Li_2SO_4	3.83	17	0.9620	0.0005
5				0.9610	0.0008
6				0.9600	0.0008
7	$MgSO_4$	3.90	15	0.9615	0.0015
8				0.9600	0.0020
9				0.9622	0.0005
10[a]	$NiSO_4$	4.19	20	0.96430	0.00005
11			50	0.96430	0.00030
12			50	0.96433	0.00015
13[a]	$CdSO_4$	3.64	35	0.9520	0.003
14				0.9510	0.003
15				0.9530	0.003
16	$ZnSO_4$	3.28	35	0.96478	0.00005
17				0.96477	0.00003
18				0.96476	0.00002
19	$CoSO_4$	3.59	32	0.96478	0.0001
20				0.96478	0.0001
21				0.96476	0.0001
22	$MnSO_4$	3.51	30	0.96478	0.00004
23				0.96478	0.00003
24				0.96478	0.00004

[a] Duplicate sets showed similar results.

expected voltage, and that the metastability of the system may persist for some time. It seemed possible that a similar cause might account for the unsatisfactory results in the above cells containing the sulfates of potassium, lithium, magnesium, and cadmium. Therefore, in order to preclude the presence of any unsuspected, solid phases in these cells, unsaturated cells were constructed for most of the salts, similar to Weston unsaturated cells. The solutions were saturated at 20° by stirring the

[1] *Loc. cit.*

soluble sulfate and lead sulfate for 3 hours, and filtering off the excess salts. These solutions were unsaturated, then, at 25°. Table III presents the results of the measurements. In the column indicating the salt used, the formulas employed indicate that the salt was not present as a solid phase.

On account of the hydrolysis evident in the cells containing saturated solutions of potassium sulfate, no unsaturated cells were constructed using this salt.

(*d*) **Evidence of the Formation of Double Salts.** *Previous Work.*—The second effort to find some explanation of the erratic results obtained with certain cells was an attempt to determine whether any secondary reaction occurred in the cells, such as the formation of double or complex salts.

Several investigators[1] have studied the double salt potassium lead sulfate, the analyses showing the formula $K_2SO_4.PbSO_4$. Brönsted states that it is a finely crystalline powder, very similar to lead sulfate; and that it is always formed (for instance, on the addition of a solution of lead nitrate to one of potassium sulfate) instead of lead sulfate if the concentration of potassium sulfate is greater than 0.4%. He states, in his studies on chemical affinity, that the chemical reaction in cells containing sodium sulfate is represented by the direct electrode reaction:

$$Pb + Hg_2SO_4 \longrightarrow PbSO_4 + 2Hg,$$

while that with the use of potassium sulfate is

$$Pb + Hg_2SO_4 + K_2SO_4 \longrightarrow K_2SO_4.PbSO_4 + 2Hg.$$

The latter arrangement, because of the formation of the double salt, gives a considerably higher electromotive force, the difference between the 2 being a measure of the energy of reaction for the formation of the double salt.

He maintains further that the thermodynamical requirement that the electromotive force be independent of the concentration is fulfilled at 22°, but not at 60–100°, and that the lower temperature probably gives the correct values.

The values obtained by the authors for cells containing potassium sulfate are somewhat lower than those of Brönsted. Furthermore, at no time was it possible to obtain with these cells such constant values as were reported by him.

Present Work.—The following methods were employed in a search for double salts in certain cells.

1. *Analytical.*—For the preparation of the suspected double salt, a 10% solution of lead nitrate was added slowly and with rapid stirring to

[1] Becquerel, *Compt. rend.*, **63**, 1 (1866); Ditte, *Ann. chim. phys.*, [5] **14**, 190 (1878); Fox, *J. Chem. Soc.*, **95**, 878 (1909); Barre, *Compt. rend.*, **149**, 292 (1909); Brönsted, *Z. physik. Chem.*, **77**, 315 (1911); Graham, *Z. anorg. Chem.*, **81**, 257 (1915).

a solution of 3 times its volume, nearly saturated with the sulfate being tested—potassium, lithium, magnesium, or cadmium. A second method was to reverse the process, adding the sulfates to the lead nitrate.

Analyses of the white products showed them to be only lead sulfate, except with the use of potassium sulfate, where the results corresponded to those found by Fox[1] for potassium lead sulfate.

2. *Microscopic.*—Examination under an ordinary microscope of the above salts, even after continued digestion in the mother liquor, revealed no characteristic difference between them and pure lead sulfate.

3. *Thermometric.*—Based on the statement of Brönsted[1] that the temperature of a saturated solution of potassium sulfate rises several degrees upon the addition of solid lead sulfate, owing to the heat of formation of potassium lead sulfate, the following method was adopted as a qualitative means of determining whether there was any thermometric indications of the formation of double salts:

Two large, insulated test-tubes, fitted with a stirrer to agitate the solution in each equally, were placed near together with a Beckmann thermometer in each. In one was placed about 25 cc. of a solution of potassium sulfate nearly saturated, and in the other an equal volume of water, all materials used being at room temperature. When the readings of temperature were changing equally, about 10 g. of solid lead sulfate was added to each tube and the readings continued. Similar experiments were made with mercurous sulfate, sulfuric acid of sp. gr. 1.15 replacing the water, since mercurous sulfate reacts with water.

On adding lead sulfate to the solution of potassium sulfate, the thermometer in the latter showed a marked rise, compared with the other instrument, which was still changing at the same rate as before. This was taken to be the result of an exothermic reaction between the lead and the potassium sulfates, and to indicate the formation of a double salt. No other combination tried, either with lead sulfate or with mercurous sulfate, showed any similar evidence of chemical reaction between the salts.

Fig. 1 is a graphical representation of the results for potassium and for lithium sulfates, in which time is plotted against change of temperature. Only constancy or inconstancy of the difference between the readings of the 2 thermometers, and not the actual values plotted, is of signi ficance.

E. Discussion.—Among the fundamentally important points in the consideration of any combination as a possibility for a standard cell are its constancy, reproducibility, value of electromotive force, temperature coefficient, and possibility of showing hysteresis.

(*a*) **Constancy.**—Evidently for the period studied, these cells may be grouped into 3 classes: first, those showing marked constancy, and, ap-

[1] *Loc. cit.*

parently, meeting the requirements of a standard (a conclusion supported by the results for the one older cell)—these include the saturated cells containing the sulfates of sodium, nickel, cobalt, manganese, and zinc;

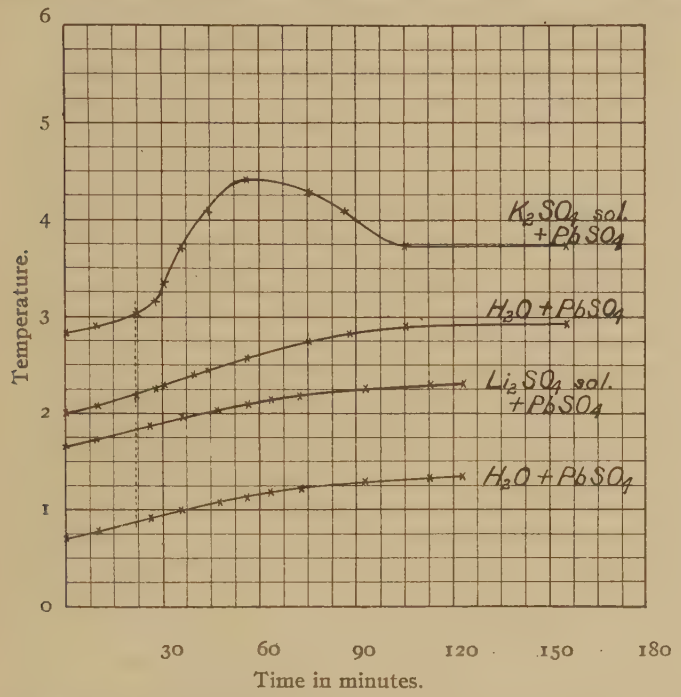

Fig. 1.—Changes in temperature of solutions of lithium sulfate and of potassium sulfate before and after the addition of solid lead sulfate to each. The dotted line indicates the time of adding the lead sulfate.

second, those showing no constancy, including saturated cells containing the sulfates of potassium, lithium, magnesium, cadmium and copper, and unsaturated cells containing the sulfates of lithium, magnesium, and cadmium; third, those constant for a short time, including unsaturated cells containing the sulfates of sodium, nickel, cobalt, manganese, and zinc.

(*b*) **Reproducibility.**—In general, the reproducibility of the cells followed closely parallel with their constancy; that is, those showing a satisfactory constancy were readily reproducible, and *vice versa*. Satisfactory cells agreed with each other within 0.02 or 0.03 millivolt. An exception to this generalization occurred in the case of cells containing copper sulfate, which seemed to agree very well but showed some inconstancy. Also certain unsaturated cells, such as those containing sodium sulfate, agreed as long as they remained constant.

(*c*) **Value of Electromotive Force.**—The electromotive force of all

constant cells was sufficiently large for the ordinary uses of standard cells, being nearly as large as that of Weston cells.

(*d*) **Temperature Coefficient and Hysteresis.**—The work of Henderson and Stegeman showed satisfactory temperature coefficients for the cells then studied. Further observations on this point and studies on the possibility of hysteresis are contemplated.

(*e*) **General.**—Brönsted's statement that the electromotive force is thermodynamically independent of the concentration of sodium sulfate seems to be somewhat confirmed, since the present saturated cells containing sodium sulfate practically agreed with the unsaturated ones (while constant). Also the electromotive force of the other constant cells, containing other salts, varied by only a small difference from the values for the cells containing sodium sulfate. For example, the 3 sulfates, cobalt, zinc and manganese, gave cells with a slightly higher electromotive force than the sulfates of sodium and of nickel; the latter 2 salts are less soluble, and hence, furnish a smaller concentration of dissolved salt.

It should be noted that the exact conditions of concentration and ionization prevailing in the systems studied are not simple. Using sodium sulfate, for instance, we have in the arm of the cell containing the amalgam the ions formed from the dissolved portion of the slightly soluble lead sulfate in the presence of the ions formed from the dissolved portion of the very soluble sodium sulfate decahydrate. On the one hand, because of the contribution of the common ion, SO_4^{--}, from the large excess of sodium sulfate, one might expect some effect of mass action, resulting in a slight decrease in the solubility of the lead sulfate, and, therefore, in a slight change from the ionization relationships obtaining for lead sulfate in water alone. Also it is probable that, with the use of a salt having a solubility differing considerably from that of sodium sulfate, we might expect some difference in the magnitude of the effect on the ionization of the lead from lead sulfate, and, hence, a slight variation in the resulting electromotive force. The solubilities of sodium and of nickel sulfates are about the same at 25° and the electromotive forces of the 2 cells practically agree. Also the sulfates of manganese, cobalt, and zinc have a considerably higher solubility, and cells containing these salts gave a higher electromotive force; but from this standpoint the manganese sulfate should have given the highest. On the other hand, it must be borne in mind that some sparingly soluble salts are more soluble in salt solutions than in water alone. The lack of accurate data on the points mentioned, for the systems studied, makes largely a matter of speculation any present attempt to formulate conclusions regarding the exact contribution of these various factors in determining the final electromotive force exhibited.

Calculation of the heats of reaction for the various cells should agree closely. On this point, using the familiar Gibbs-Helmholtz equation,

$$Q = nF\ (E - T\ dE/dT)\ 0.2387,$$

Stegeman[1] made 2 calculations of the heat of reaction; for cells containing sodium sulfate the error was 0.86%, and for those containing zinc sulfate 0.19%, compared with the value calculated from thermochemical data for the reaction

$$Pb + Hg_2SO_4 \longrightarrow PbSO_4 + 2Hg.$$

Similar calculations for the other constant cells should agree closely with the above, indicating that these salts probably do not function in the above reaction, and that it is the only appreciable one occurring.

Conversely, since this Gibbs-Helmholtz equation gives a means of calculating the algebraic sum of the heats of all reactions proceeding when a cell gives a current, if some combination, such as the ones studied, gives an electromotive force appreciably different from those of the constant cells, probably the above reaction is not the only one taking place. Cells containing potassium sulfate, for example, gave an electromotive force considerably higher than that obtained using sodium sulfate, indicating a secondary reaction whose energy is added to that of the primary reaction. The process of this secondary reaction, forming a double salt, is exothermic, and the heat of this reaction corresponds with that calculated from the increase in electromotive force.[2]

In the case of the cells containing copper sulfate there is evidently some chemical action other than the one between lead and mercurous sulfate, since the electromotive force produced is approximately $1/3$ that of the constant cells. Copper is below lead in the electromotive series, and, therefore, one would expect a displacement of the copper in the copper sulfate by the lead of the amalgam to form more lead sulfate. This reaction would be continuous until equilibrium were reached because of exhaustion of the lead in the amalgam or of the copper sulfate. Because of the comparatively large excess of copper sulfate, the lead should be exhausted first, and the displaced copper should form an amalgam. This would leave as the essential constituents of the reacting system the following arrangement:

$$Cu.Hg \mid CuSO_4.5H_2O \parallel Hg_2SO_4 \mid Hg.$$

In this system would be also the lead sulfate originally added in addition to that formed by the displacement of the copper from some of the copper sulfate. The essential reaction of the cell would now be represented by the equation

$$Cu + Hg_2SO_4 \longrightarrow CuSO_4 + 2Hg.$$

[1] Stegeman, *Dissertation*, Ohio State University, 1917.

[2] Brönsted, *loc. cit.*

The probable correctness of the latter conclusion seems to be supported by the work of McIntosh[1] on a cell constructed according to the arrangement

$$Cu \mid CuSO_4.5H_2O \parallel Hg_2SO_4 \mid Hg.$$

For this combination he obtained an electromotive force of 0.3580 volt at 22° as a mean for 4 cells; using his temperature coefficient, this value becomes 0.35605 volt for 25°. The mean value for the authors' 3 cells is about 0.3487 at 25°. It should be borne in mind, however, that McIntosh used a pure copper electrode, while the present electrodes are copper amalgams.[2] Also he washed his mercurous sulfate with water, which seems a questionable procedure in view of later work with this compound for use in Weston and in Clark cells.

Part III. Summary and Conclusions.

A.—A galvanic cell constructed early in 1917 according to the arrangement

$$Pb.Hg \mid PbSO_4 \parallel Na_2SO_4.10H_2O \parallel H_2SO_4 \mid Hg,$$

in which Pb.Hg represents a saturated amalgam, and $PbSO_4$, $Na_2SO_4.10H_2O$, and Hg_2SO_4 represent saturated solutions, has been measured and found to give the same electromotive force as new cells of the same construction, and to have a constant value throughout the present work.

B.—Similar saturated cells have been studied using, in addition to sodium sulfate, the well-defined, soluble sulfates of nickel, cobalt, zinc, manganese, potassium, lithium, magnesium, cadmium and copper. The observations on these cells indicate:

(1) A confirmation, in general, of the work of Henderson and Stegeman on the constancy and reproducibility of cells containing sodium sulfate.

(2) That saturated cells containing the sulfates of nickel, cobalt, zinc, or manganese are substantially as reproducible and as constant as those containing sodium sulfate. This constancy is usually attained within 4 or 5 days, after preparation, and, for the time studied, these cells appear to possess the characteristics necessary for a standard cell.

(3) That the electromotive force of the constant cell seems to be nearly independent of the soluble sulfate used. The values for cells containing sodium sulfate or nickel sulfate practically coincide; while those for cells containing the sulfates of cobalt, zinc, or manganese are very close together, but slightly higher than the first 2.

(4) That saturated cells containing the sulfates of lithium, magnesium, or cadmium are neither reproducible nor constant, although their electromotive force is of approximately the same magnitude as that of the constant cells.

[1] *J. Phys. Chem.*, **2**, 189 (1898).

[2] Assuming a lead amalgam of 3.1% lead to start, and the complete exhaustion of this lead to displace copper, we should then have an amalgam containing 0.96% copper.

(5) That saturated cells containing potassium sulfate are also neither constant nor reproducible. The mercurous sulfate in them was distinctly hydrolyzed, and their electromotive force was markedly higher than that of the other cells.

(6) That saturated cells containing copper sulfate agree well among themselves but are not constant. Their electromotive force is approximately one-third that obtained for the other cells, indicating that the system contributing the electromotive force has been changed, as a result of the obvious secondary reaction in which the lead of the amalgam displaces copper and the copper goes to make up the amalgam, to that represented by the arrangement,

$$Cu.Hg \mid CuSO_4.5H_2O \parallel Hg_2SO_4 \mid Hg.$$

C.—Unsaturated cells containing the sulfates of sodium, zinc, nickel, cobalt, and manganese have been studied, and the observations on them indicate:

(1) That they are as reproducible as the corresponding saturated cells.

(2) That they give practically the same electromotive force.

(3) That they are constant for a time and then begin to exhibit a decreasing electromotive force.

D.—Two lines of investigation have been conducted in an effort to locate the cause of the unsatisfactory results with saturated cells containing the sulfates of potassium, lithium, magnesium, or cadmium:

a. Unsaturated cells containing the sulfates of lithium, magnesium and cadmium have been studied, and the observations indicate:

(1) That their electromotive force approximately equals that of the corresponding saturated cells.

(2) That these cells are equally unsatisfactory.

(3) That the erratic values of the saturated cells are probably not, therefore, the result of the coexistence in the cell of the anhydrous sulfate and a hydrate or of different hydrates, as has been noted in certain Clark cells.

b. Evidence was sought, by means of analytical, microscopic, and thermometric methods, which would indicate whether the unsatisfactory results might be caused by the formation of double salts in the cells. The indications were:

(1) That analytically, there is evidence for the formation of only one double salt, potassium lead sulfate.

(2) That microscopically, no conclusions of value are possible.

(3) That thermometrically, the evidence points to the formation of only one double salt, potassium lead sulfate.

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AUTOBIOGRAPHICAL FACTS.

Born on a farm near Conneaut Lake, Pa., October 25, 1893, my training and environment were those of the country until the time of entering college. Seven years were spent in the country school near the home farm, where the regular work was completed in April, 1907. My high school course began at Conneaut Lake in the autumn. This continued three years, during which time I completed the four years' college preparatory course, graduating in 1910. The following September I entered Allegheny College, Meadville, Pa., enrolling in the scientific course. The end of the first year found me undecided regarding the most desirable course of study to pursue. However, a place for thinking over this indecision seemed to present itself in an opportunity to teach; accordingly the winter of 1911–12 was spent teaching a country school. At the end of that time my mind was fully made up to study chemistry, and I returned in 1912 to Allegheny college, where I graduated in 1915, having taken practically all the available chemical courses. Arrangements were then made to take up graduate work in chemistry at The Ohio State University. By working there during several summer sessions, the requirements for the degree of Master of Science were completed in 1916, and those for the degree of Docotor of Philosophy in 1919. During the first three years of this graduate study, I served as an assistant instructor in the Department of Chemistry, becoming a full-time instructor the fourth year.